

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) University of California, San Diego, Marine Physical Laboratory of the Scripps Institution of Oceanography San Diego, California 92132		2a. REPORT SECURITY CLASSIFICATION Unclassified	
3. REPORT TITLE ORIGIN OF THE LOW FREQUENCY SOUND ABSORPTION IN SEA WATER		2b. GROUP 492858 (1)	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Summary <i>Sea water - Acoustic prop.</i>			
5. AUTHOR(S) (First name, middle initial, last name) Ernest Yeager, F. H. Fisher, John Miceli and Robert Bressel			
6. REPORT DATE 15 December 1972	7a. TOTAL NO. OF PAGES 3	7b. NO. OF REFS 16	
8a. CONTRACT OR GRANT NO. N00014-69-A-0200-6002, NR 260-103 and N00014-67-A-0404-0004, Project 384-305		9a. ORIGINATOR'S REPORT NUMBER(S) MPL-U-63/72	
		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SIO Reference 72-84	
10. DISTRIBUTION STATEMENT Distribution is unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office of Naval Research	
13. ABSTRACT Temperature-jump measurements in sea water over the time domain 10^{-5} to 10^{-2} sec reveal a single relaxation of $150\mu\text{sec}$ at 9.7°C , which appears to correspond to the ~ 1 kHz relaxation found from long range sound propagation. Laboratory measurements indicate the relaxation to originate from boron with the $\text{B}(\text{OH})_3 - \text{B}(\text{OH})_4$ equilibrium the likely relaxing process. This research was sponsored by the Office of Naval Research.			

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Sponsored by
Office of Naval Research
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SIO REFERENCE 72-84

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MPL-U-63/72

ORIGIN OF THE LOW FREQUENCY SOUND
ABSORPTION IN SEA WATER†

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ABSTRACT

Temperature-jump measurements in sea water over the time domain 10^{-5} to 10^{-2} sec reveal a single relaxation of $150\mu\text{sec}$ at 9.7°C , which appears to correspond to the ~ 1 kHz relaxation found from long range sound propagation. Laboratory measurements indicate the relaxation to originate from boron with the $\text{B}(\text{OH})_3 - \text{B}(\text{OH})_4$ equilibrium the likely relaxing process. This research was sponsored by the Office of Naval Research.

Sea water exhibits large excess acoustical absorption of frequencies below 100 kHz because of a chemical relaxation involving magnesium sulfate with a relaxation frequency of ~ 70 kHz, corresponding to a relaxation time $\tau = 2.3\mu\text{sec}$.^{1/} From analysis of long range acoustic propagation in the deep sound channel (depth 1300 m at $\sim 4^\circ\text{C}$), Thorp^{2/} has concluded that sea water has an additional relaxation at ~ 1 kHz ($\tau = \sim 160\mu\text{sec}$) which further increases the absorption by a factor of ~ 10 over the magnesium sulfate absorption. Long range sound propagation studies in Lake Superior and Lake Tanganyika have also been reported^{3/} to yield similar excess absorption at frequencies below 1 kHz but

these absorption data are far less certain and remain to be confirmed.

The acoustical absorption of sea water has not been measured in the laboratory at such low frequencies because of the very small attenuation coefficients (i.e., 10^{-1} dB/km at 1 kHz). Other relaxation methods, however, can be used to obtain information concerning the origin of this low frequency acoustic relaxation. This communication reports laboratory measurements on real^{4/} and synthetic sea water by the temperature-jump^{5/} relaxation method, which confirms the existence of a relaxation in sea water of the proper relaxation time and identifies the boric acid-borate system as responsible for this low frequency relaxation.

The relaxation spectrum of sea water was examined in the range 10^{-5} to 10^{-2} sec with temperature-jump apparatus (Messanlagen Studiengesellschaft)^{5/} in which a temperature rise of $\sim 3^\circ\text{C}$

† Joint contribution from the Scripps Institution of Oceanography, University of California, San Diego and Case Western Reserve University, Cleveland, Ohio.

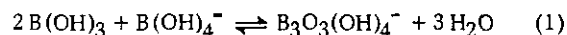
is produced in $< 10^{-6}$ sec through a condenser discharge through the solution. The subsequent relaxation is followed optically by means of a hydrogen ion sensitive color indicator (2.0×10^{-5} M phenol red unless otherwise noted). Only one relaxation was found with $\tau = 107$ μ sec at 25.5°C . Modification of the pH of the sea water by small additions of HCl or KOH had no effect on the relaxation time over the pH range 7.2 to 8.7. At a pH of 9.46, the relaxation time increased to 153 μ sec, using 2.0×10^{-5} M thymol blue as the indicator to give adequate sensitivity at the higher pH (see Table I).

Dilution of sea water by a factor of two with a solution consisting of 0.7 M NaCl plus sufficient NaHCO_3 to yield a final pH 7.66 increased τ to 160 μ sec at a pH of 7.5 and 25.5°C . For a similar dilution by 5 fold, τ increased to 460 μ sec. Upon restoring the total boron concentration to the normal sea water value of 4×10^{-4} M by adding $\text{Na}_2\text{B}_4\text{O}_7$, the relaxation time of the 5-fold diluted sea water decreased from 460 to 118 μ sec, a value essentially the same as that of undiluted sea water. Lowering the temperature to 9.7°C increased the relaxation

time of undiluted sea water to 150 μ sec, which compares favorably with the value of 160 μ sec calculated from Thorp's analysis from long range acoustic propagation data at $\sim 4^\circ\text{C}$.

To establish further that the boric acid-borate system is responsible for the observed relaxation, synthetic sea water was prepared according to the Lyman-Fleming formulation^{6/} but without any borates or boric acid added. This formulation includes only constituents at concentrations above 1 ppm.^{7/} Such boron-free synthetic sea water did not exhibit any relaxation in the temperature-jump apparatus in the 10^{-5} to 10^{-2} sec range. Upon addition of sufficient boric acid to duplicate the total boron concentration in real sea water, the relaxation reappeared with $\tau = 92$ μ sec. Similar results are to be expected with the addition of sodium tetraborate in place of boric acid since the tetraborate anion is in equilibrium with the $\text{B}(\text{OH})_4^-$ anion and boric acid. Only the pH will differ and then only by a few tenths of a pH unit over a range where the relaxation time appears to be relatively insensitive to pH in sea water.

Anderson et al.^{8/} have examined the relaxation spectra of boric acid in 0.1 M NaClO_4 solutions using the temperature-jump method. The total boron concentrations, however, were in the range 0.06 to 0.6 M, which is much higher than in sea water or used in the present study. These authors observed a concentration dependent relaxation time with a value of 12.9 msec at 0.06 M total boron concentration at 25°C . At lower concentrations, this relaxation time should become even longer and hence be far longer than the sea water acoustic relaxation time. Anderson et al. assigned the relaxation which they observed to the reaction



At the concentrations and pH involved in their studies, the concentration of the polymeric species $\text{B}_3\text{O}_3(\text{OH})_4^-$ as well as boric acid should be appreciable. At the total boron concentrations and pH of sea water, however, the equilibrium constant data of Ingri et al.^{9,10/} indicate that the concentrations of the various polymeric borates [e.g., $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$] should be far too small to account for the excess acoustic absorption of sea water below 1 kHz or the relaxation effects observed in the present work.

Knoche^{11/} has proposed that the relaxation of an aluminum sulfate complex is responsible for the excess sound absorption in sea water below a few kilohertz. If the excess absorption is calculated using the rate constants obtained by Kalidas, Knoche and Papadopoulos^{12/} and the value listed by Goldberg^{7/} for the concentration of aluminum in sea

TABLE I. Relaxation times measured with the temperature-jump method^a

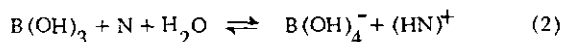
A. pH dependence of τ in sea water ^b at 25.5°C				
pH	7.17	7.66	8.54	9.46
$\tau(\mu\text{sec})$	107	107	107	153
B. Concentration dependence of τ at 25.5°C in sea water ^b diluted with 0.7 M NaCl and sufficient NaHCO_3 added to adjust the final pH to 7.66				
% (volume) sea water	100	50	20	
$\tau(\mu\text{sec})$	107	164	456	
C. Temperature dependence of τ in sea water ^b				
temperature	25.5°C		9.7°C	
$\tau(\mu\text{sec})$	107		150	

^a Temperature rise: $\sim 3^\circ\text{C}$; indicator: 2×10^{-5} M phenol red except at pH 9.46, 2×10^{-5} M thymol blue. Temperatures listed are values following temperature rise.

^b Sea water sample obtained from Standard Sea Water Service, I.A.P.S.O., Charlottenlund, Denmark, Chlorinity: 19.375‰, 12-13/6/1971.

water (0.01 mg/liter or 4×10^{-7} M), the predicted excess absorption to be expected is far too small to explain the observed absorption. Further, the omission or addition of Al^{3+} at 4×10^{-7} M to the artificial sea water had no effect on the observed relaxation with the temperature-jump method.

The chemical process responsible for the excess acoustic absorption in sea water and the relaxation observed in the present study is believed to involve an acid-base equilibrium between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ of the form



where N is a Lewis base such as OH^- or CO_3^{2-} . Reaction 2/ may proceed through two steps as suggested by Muetterties^{13/} with the slow step involving the rearrangement from a trigonal to tetrahedral distribution of oxygen around boron. This rearrangement should result in a substantial contribution to the activation free energy for the acid-base conversion with the result that the overall $\text{B}(\text{OH})_3 - \text{B}(\text{OH})_4^-$ conversion should be much slower than expected on the basis of simple diffusion control.

In sea water, reaction 2 will be coupled to other processes involving OH^- and H^+ ions, including the $\text{CO}_3^{2-} - \text{HCO}_3^- - \text{H}_2\text{CO}_3$ equilibria^{14,15/} which in turn are coupled to such processes as the formation of MgCO_3 and CaCO_3 complexes.^{14,15/}

The complete analysis of the boric acid-borate relaxation in sea water is expected to be quite complicated and will be the subject of a future investigation. A preliminary analysis, however, indicates that the data in Table I are reasonable for reaction 2 as the slow relaxing process.

While the relaxation time from the temperature-jump study corresponds to that from the long range acoustic propagation studies in sea water, the temperature-jump method does not yield information concerning the volume change (ΔV) of the relaxing process. Such is needed to calculate the excess acoustical absorption to be expected from the relaxation. Efforts are in progress to determine ΔV using the pressure shock wave relaxation method^{16/} with the conductivity read-out normally used with this method replaced with an optical read-out similar to that involved in the temperature-jump studies.

ACKNOWLEDGMENTS

This research has been supported by the Office of Naval Research. The authors express appreciation to Prof. J. Stuehr of Case Western Reserve University for the use of temperature-jump equipment in his laboratory and to Dr. H. Hoffman for his help in the design and use of the pressure-shock apparatus.

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